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# Local impedance spectra of organic coatings

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ABSTRACT

An atomic force microscopy (AFM) based approach to local impedance spectroscopy of organic coatings is presented. The impedance measurements were performed in a stationary regime with the AFM tip positioned on a surface of epoxy coated steel substrate. A set of voltage perturbation signals was applied between the tip and the substrate and impedance spectra were recorded in the frequency by frequency mode. The results were compared with the classical global impedance measurements and found to be consistent and complementary with those. They supplied additional information as far as identification and localization of coating defects is concerned.



## 1. Introduction

Electrochemical impedance spectroscopy (EIS) became one of the fundamental tools for non-destructive evaluation of organic coatings [1–7]. It opened a possibility of following the changes occurring inside the film as well as at the film/substrate interface, especially when no macroscopic evidence of degradation is evident. Thus it offers an opportunity to predict lifetime, monitor behaviour of the coating and to react earlier in case of failure.

The next step was to focus on microscopic phenomena in the coatings as they determine macroscopic performance of the protective film. To overcome the limitation of classical impedance measurement, the result of which is averaged over relatively large area, typically of $cm^2$ or $mm^2$ order, local variants of impedance measurement have been investigated by many scientists.

One of the approaches to local electrochemical impedance spectroscopy (LEIS) was presented by Dehri et al. who applied a number of cylindrical cells engulfing the area of 50.3 $mm^2$ to evaluate coil-coated film on galvanized steel as a function of a distance from the cut edge [8]. Detection and mapping the location of heterogeneities leading to coating failure were the objectives of local electrochemical impedance studies of Wittmann and co-workers [9] as well as Mierisch and others [10,11] which successfully employed a five-electrode system utilizing a split micro-reference electrode. This method was also implemented by Taylor to observe extrinsic-type coating defects associated with processing and manufacture as well as individual intrinsic-type failures [12]. Zhong et al. performed local electrochemical impedance measurements in the five-electrode configuration on coated steel to investigate localized corrosion under defective coating in a near-neutral pH solution [13]. Anomalous impedance variations of epoxy, alkyd and polyurethane coated panels as a function of exposure time in a sodium chloride solution were discussed by Macedo et al. who also employed the five-electrode system [14]. Stretching-induced defects occurring at the interface between spherical zinc particles and the epoxy binder were identified by Kluppel and co-workers who employed a set-up comprised of an electrochemical microcapillary cell in a three-electrode arrangement and miniaturised linear stretching device for local impedance measurement [15]. A review on local electrochemical impedance spectroscopy developments was provided by Huang et al. [16].

However, the majority of the approaches applied so far require the measurements to be carried out in an electrolyte, which is not always a convenient solution. Moreover, unequivocal results are typically obtained with these techniques only when there is a through-the-coating defect and bare metal is exposed to electrolyte, for instance through a pinhole.

Accordingly, we decided to apply to coatings the methodology originally proposed by Kalinin et al. for investigation of transport behaviour of individual grains and grain boundaries in polycrystalline ZnO [17]. It was also adopted by O'Hayre in the field of solid polymer electrolytes, polycrystalline ZnO varistors and microscale test patterns of different electrical behaviour [18,19]. This approach makes it possible to perform local impedance imaging [20] and spectroscopy using contact atomic force microscopy (AFM) mode. The measurements are conducted without the

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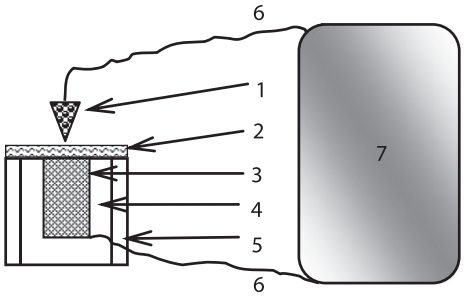


**Fig. 1.** Scheme of the investigated specimen: 1-AFM tip, 2-epoxy coating, 3-steel substrate, 4-immobilizing resin, 5-plastic cylinder, 6-electrical connections, 7-AFM set-up (topography measurements)/Parstat 2236 workstation (local impedance measurements).

presence of electrolyte and thus they are not electrochemical in character. This method was successfully applied for investigation of inter-granular corrosion of stainless steel [21]. In this paper we present the first full local impedance spectra obtained for organic coatings on steel.

## 2. Material and methods

The investigation was performed on epoxy coating deposited on circular carbon steel substrate (1 mm diameter) by air spray technique (Fig. 1). Average coating thickness was $20 \pm 3$ μm. The sample was exposed to UV radiation for 500 h (the radiation was produced by a 320 nm wavelength lamp providing the radiation intensity of 3.6 W/m$^2$ at a distance of 1 m).

The following measurements were carried out in order to evaluate the coating condition at a particular stage of the exposure: (i) topography profile acquisition with AFM contact mode, (ii) local impedance spectroscopy measurements with AFM set-up and (iii) global classical impedance measurements.

Surface topography measurements were performed with the SPM Ntegra Aura system by NT-MDT Co. The investigations were carried out in dry conditions, without immersion in the electrolyte. Scanning by the tip mode was selected and the maximum scan area was 8100 μm$^2$ (90 μm × 90 μm). Scanning frequency was 1 Hz. Measurement resolution was 0.35 μm (scanned distance 90 μm divided by a number of pixels in a line − 256). All the scans were collected for the set point providing the contact force of 6 μN. The parameters of applied silicon AFM tip coated with platinum are gathered in Table 1.

The resulting current was recorded and mapped according to an instantaneous position of the tip. Nova software by NT-MDT Co. was employed for topography and spreading resistance image registration, processing and analysis.

Based on topography images some characteristic points on the sample surface (intact area, surface depressions and elevations, cracks etc.) had been selected where local impedance spectra were recorded. Impedance measurements were performed in the stationary regime with the tip positioned in the localizations of interest. The tip was brought into contact with the surface by enabling the feedback and the measurements were performed for the assumed contact force applied. Following the impedance

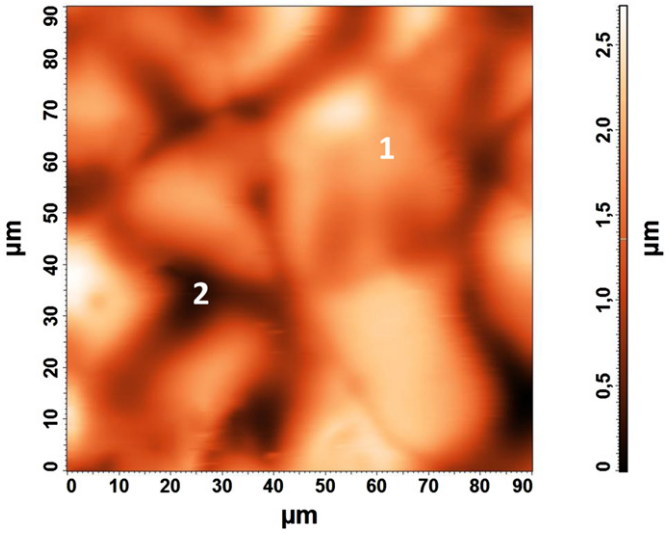


**Fig. 2.** Topography image of epoxy coating surface prior to UV exposure. The numbers indicate the places, where local impedance spectra were recorded.

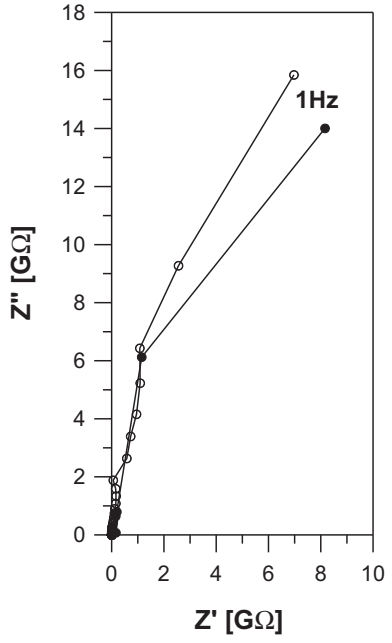


**Fig. 3.** Exemplary impedance spectra prior to UV exposure: (○) global spectrum, (●) local spectrum recorded in places marked as 1 and 2 in Fig. 2.

spectrum measurement in the frequency by frequency mode the feedback control was turned off and the tip was transferred to another position on the surface. Impedance measurement set-up consisted of the Parstat 2236 workstation configured in two-terminal measurement mode. One terminal was connected to the coated specimen whereas the other was in contact with the conductive layer of the AFM probe by means of dedicated holder.

**Table 1**
Parameters of the tip CSG10/Pt by NT-MDT utilized in the studies.

| Chip size [mm] | Tip height [μm] | Tip curvature radius [nm] | Tip side coating | Cantilever length [μm] | Cantilever width [μm] | Cantilever thickness [μm] | Resonant frequency [kHz] | Force constant [N/m] |
|---|---|---|---|---|---|---|---|---|
| 3.4 × 1.6 × 0.3 | 14–16 | 15–20 | Pt 20 nm | 225 | 30 | 0.5–1.5 | 8–39 | 0.01–0.5 |